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Field Portable Petroleum Analysis for Validation of the Site Characterization and Analysis Penetrometer System Petroleum, Oil and Lubricant Sensor

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ABSTRACT

A petroleum, oil and lubricant (POL) sensor for the Site Characterization and Analysis Penetrometer System (SCAPS) has been developed by the Tri-Services (eg. Army, Navy and Air Force) to characterize the distribution of POL contaminants on military sites. The sensor is based on the detection of POL contaminants using a laser induced fluorescence (LIF) spectrometer. The SCAPS POL sensor has been shown to be a valuable tool for the rapid screening of POL contamination in the subsurface. However, many factors can affect the LIF response of a particular fuel at a particular site. These include fuel type, age of spill (e.g. weathering) and soil type. The LIF sensor also detects fluorescence from any naturally occurring fluorophores, including humic substances and fluorescent minerals. These factors lead to the development of an independent procedure for the verification of the POL sensor response. This paper describes a field portable total recoverable petroleum hydrocarbon (TRPH) method based on EPA Method 418.1 and its application to on site validation of the SCAPS POL sensor response at a number of contaminated sites.

INTRODUCTION

The SCAPS POL sensor has been developed at Waterways Experiment Station (WES) as part of a Tri-Service research program on methods for rapid site characterization. The POL sensor is based on using laser induced fluorescence for rapid in-situ detection of POL contaminants. The POL sensor has been integrated via fiber optic cables into a standard geophysical cone penetrometer creating an instrument that simultaneously delineates subsurface stratigraphy and POL contamination.

The SCAPS POL sensor has been field tested at a number of DoD installations and has demonstrated the utility of the LIF technique for the in-situ detection of POL contaminants. These tests have also identified a need for verification of the SCAPS LIF response by traditional site characterization methods (e.g. soil sampling and laboratory analyses). Verification of LIF response is necessary for accurate interpretation of LIF data (i.e. identification of non-POL fluorescence) and regulatory acceptance of this new technology.

A field portable method has been developed for on site analysis of POL contaminants in soils. This paper describes the development and validation of a modified EPA Method 418.1 and its application to field portable POL analysis for on-site verification of the SCAPS LIF response.

METHODS

Laboratory spiked soil samples were prepared using a procedure developed at WES (Lee et al 1994). Soils fortified in the lab were Fisher Sea Sand (Fisher Scientific, Inc.), Columbus Air Force Base soil (2.5% clay), and China Lake Naval Base soil (5% clay). These soils were spiked at 100, 300, 1000, 3000 and 10000 mg/kg with each of the four fuels investigated (diesel fuel

marine, #2 diesel fuel, JP-4 and unleaded gasoline). Soil samples were obtained at field sites using either a direct push soil sampler (Mostap Model 35) deployed using the SCAPS truck or a drill rig equipped with a hollow stem auger and split spoon sampler. Field samples were obtained from PO contaminated sites at Sierra Army Depot, Honey Lake, CA; Alameda Naval Air Station, Alameda, CA; Marshalltown Coal Gasification Site, Marshalltown, IA; Ft. Riley, KS; York, NE and Atlantic IA. All field samples were homogenized in the field by mixing with a stainless steel spatula in a stainless steel pan. Samples were placed in precleaned 250 or 500 mL glass jars equipped with teflon lined caps and stored at 4°C until analyzed.

Soil analyses for TRPH were performed in the laboratory using EPA Method 418.1 (U.S. EPA, 1983) and in the field using the on site method developed during the current study. Both methods are based on solvent extraction (1,1,2-trichloro-1,2,2-trifluoroethane, Freon 113) of petroleum from the soil and quantification of the petroleum present in the extract by infrared (IR) spectroscopy. Initially, 10 g of soil a weighed and mixed with 2 g Na₂SO₄ to remove moisture. This sample is then mixed with 1 g silica gel to remove natural fatty acids and waxes. EPA Method 418.1 solvent extraction is then carried out with Freon 113 used in either a soxhlet extraction procedure or with an ultrasonic cell disrupter operated at 300 W. The field portable TRPH procedure uses the same solvent but the extraction is carried out in an ultrasonic bath (120 W).

The SCAPS LIF response was obtained for each homogenized soil sample in the field by pressing the soil against the sapphire window of the SCAPS POL sensor probe and collecting ten replicated emission spectra (Lee et al. 1994). This procedure was carried out in triplicate for each soil sample investigated. Standard operating procedures for the SCAPS POL sensor have been described elsewhere (Apitz et al. 1992, Lee et al. 1994.).

RESULTS AND DISCUSSION

Comparison of EPA Method 418.1 with the field portable method

Investigations were carried out to compared TRPH recovery efficiency of the field portable method and EPA Method 418.1. Experiments were performed with samples fortified in the laboratory (Lee et al. 1994) and soil samples obtained from contaminated field sites. A variety of soils and contaminant types were investigated. Soils included sands, clays and silty soils. Contaminants investigated during this study included unleaded gasoline (UNL), JP-4, #2 diesel and diesel fuel, marine (DFM) for laboratory constructed soils and #2 diesel fuel, coal tar, UNL and petroleum refinery waste for the field samples.

The data set from the analysis of the laboratory fortified soils and the field samples were pooled and a linear regression analysis was performed. These data yielded a strong correlation ($r^2 = 0.93$, slope 0.97) between these two petroleum contamination measures (Figure 1). It should be noted that, both the laboratory and field samples yielded strong linear correlations when analyzed separately ($r^2 = 0.95$, $n = 216$ and $r^2 = 0.94$, $n = 82$, respectively). The pooled data set ($n = 298$) contains a wide variety of both soils (sands through clays) and POL contaminants (six different contaminant types). The linear correlation indicated by the regression analysis and the slope near 1.0 (Figure 1) demonstrate the equivalence of the two procedures for measuring the POI contamination of soils.

Field Portable TRPH for Validation of SCAPS LIF Response

The field portable TRPH method was developed for on site validation and calibration of the fluorescence response obtained by the SCAPS POL sensor. The feasibility of on site validation and calibration of the LIF response with the field portable TRPH method was investigated at six locations: Sierra Army Depot, Alameda Naval Air Station, Marshalltown, IA coal gasification site Atlantic, IA coal gasification site, York, NE coal gasification site and Ft Riley Kansas.

Qualitative Data Interpretation. The first application of the results of TRPH analysis carried out in the field for POL sensor verification is a qualitative comparison of the TRPH results with the LIF response for the verification samples. This procedure involves the evaluation of the frequency of POL sensor false positive and false negative response based on the TRPH analyses. A false positive POL sensor response would be assigned to a sample that yielded LIF response (above site background), while the TRPH analysis indicated no POL contamination. False negative LIF response. It should be noted that the LIF background response varies from site to site and this must be considered during the data reduction for the LIF sensor response.

Various techniques have been used to assign the fluorescence background observed with the LIF sensor at a particular site. These include (1) measuring the natural LIF response of a site soil sample that is known to be contaminant free and (2) reading the LIF response from a flat region of a panel plot (LIF versus depth of penetration plot) and plotting the low level LIF responses as a histogram to locate the median low level response. The later method assumes that, at low response, the distribution of LIF response is Gaussian and the median of this curve can be used to assign the site background. This is the procedure that was used to determine the background in the current study.

Another consideration when assigning a LIF response as negative or false negative is the detection limit of the LIF sensor. Although the LIF sensor response is subject to soil matrix effects (Apitz et al. 1992), it is always less sensitive than the TRPH procedure (15 mg/kg) for the POL contaminants investigated here. Therefore, there is a TRPH concentration range where the LIF sensor will indicate background response and the field portable TRPH sensor will indicate the presence of contaminant. This concentration range should be considered below detection limit for the POL sensor and the LIF response for these samples should be assigned as a true negative. For the POL contaminates and soil conditions investigated in this study, the limit of detection (LOD) for the LIF sensor is 100 mg/kg or higher. Therefore, the value of 100 mg/kg will be used as the LOD for this discussion. Since the actual site LOD may be higher, this value is conservative and may cause the assignment of more false negative LIF responses than are truly present in the data.

The results of the LIF and field portable TRPH analyses of the field samples obtained at the six sites investigated are summarized in Table 1. The assignment of true positives and negatives, as well as false positives and negatives, assumes that samples with POL contaminants measured as TRPH (≥ 100 mg/kg) are considered truly contaminated. These data ($n = 227$) indicate that the SCAPS POL sensor was able to detect the presence of POL contamination 86 % of the time it was present in the soil samples as measurable TRPH (≥ 100 mg/kg). Only 14 % of the cases represented false negatives (LIF response at background and TRPH ≥ 100 mg/kg). The high rate of true positives and low rate of false negatives for this data set supports the utility of the SCAPS POL sensor as a field screening tool. However, 69 % of the samples that were negative by the LIF sensor were true negatives by the field portable TRPH procedure. This means that 31 % (31 of 99) of the samples that contained ≤ 100 mg/kg by the field portable TRPH method had LIF response above the background response (false positives).

Mineral Fluorescence. The high occurrence of false positive LIF response in this data set demonstrates the need for a technique to verify the LIF sensor response in the field. As discussed earlier, the potential for false positive fluorescence response exist due to the occurrence in soils of fluorescent minerals and other non-POL fluorophores. All false positive LIF responses at Sierra Army Depot (Table 1, $n = 12$) were due to the fluorescent mineral calcite. The occurrence of mineral fluorescence at this site was confirmed by two methods. In addition to the use of the field portable TRPH procedure to confirm the presence or absence of POL contamination, soil samples that yielded LIF response, but no TRPH response were analyzed off site by X-ray diffraction. The X-ray analyses indicated that the samples contained the fluorescent mineral calcite (Lee et al. 1994). The presence of mineral fluorescence was suspected for the Sierra Army Depot false positive

samples due to an observed shift in the wavelength of the peak fluorescence for these samples relative to the wavelength of peak fluorescence of the POL contaminated soils. However, it should be noted that the lack of detectable TRPH in the field led to the collection of soil samples for X-ray diffraction.

The fluorescence emission spectrum for the #2 diesel fuel present at Sierra Army Depot was significantly different from that of the mineral calcite (Figure 2). The #2 diesel fluorescence spectrum peaked in the 400 nm range while the calcite fluorescence spectrum peaked in the 450 nm range. The use of chemometric and neural network pattern recognition computer programs to differentiate POL fluorescence response from naturally occurring mineral and humic fluorescence response (Andrews and Lieberman, 1991). The use of software based detection of mineral and humic fluorescence is the subject of continuing research within the Tri-Service SCAPS program. However, until these systems are developed and fully tested, it will be necessary to rely on field laboratory petroleum analyses to identify the false positive POL sensor response.

Quantitative Data Interpretation. Previous studies with laboratory fortified soils have shown strong linear correlations between POL concentration and LIF response (Apitz et al. 1992, Lee et al. 1994). These studies include both sand and clay soils and a variety of different POL contaminants. The correlation coefficients for regression of the LIF response with the POL contaminant concentration in these studies were ≥ 0.95 . However, samples constructed in the laboratory do not account for the numerous potential effects of soil matrix and POL weathering that can influence the POL fluorescent response (Apitz et al. 1992). It is therefore imperative to investigate field contaminated soils in order to build a sufficiently large database to understand and predict the relationship between LIF response and TRPH concentration over a wide range of soil and POL contaminant types.

The relationship between LIF response and the field portable TRPH for the samples obtained at Sierra Army Depot have been discussed in detail by Lee et al. (1994). Twenty two soil samples were obtained for verification and calibration studies at this site. As discussed earlier (Table 1), there were a significant number (12) of mineral based false positive LIF responses in this data set that were identified by the field portable TRPH procedure. When these data points were removed, linear relationship between the field portable TRPH and the LIF response was observed ($r^2 = 0.88$, $n = 10$). A similar correlation ($r^2 = 0.80$, $n = 37$) was obtained for the regression analysis of data from a #2 diesel contaminated site at Ft. Riley (Figure 3). The linear relationships obtained for these two field sites support the feasibility of the field portable TRPH for on site calibration of the POL sensor with actual field contaminated soils.

The Sierra Army Depot and Ft. Riley sites each contained only a single POL contaminant (#2 diesel in both cases) that were located in relatively homogeneous soil strata (sand) at each site. The Marshalltown Coal Tar Site (MCTS), investigated as part of the U.S. Department of Energy Expedited Site Characterization Demonstration program was a significantly more complex site. As implied by the name, this site was a former coal gasification plant in Marshalltown, IA that had been contaminated with coal tar waste from approximately 1900 to about 1940. Coal tar is not a petroleum product but is a contaminant that is very amenable to detection by LIF since up to 50 % (by weight) of coal tar is highly fluorescent polycyclic aromatic hydrocarbons (PAHs) (Lee et al. 1992, Leohr et al. 1992). This site was more complex than the two sites discussed previously because it appeared to have multiple contaminant types located in two different soil types (sand and clay).

The validation samples collected at MCTS indicated that the POL sensor was able to detect the coal tar contamination at this site (Table 1). Coal tar contamination is a significant problem at more than 3000 sites identified in the U.S. (Leohr et al. 1992). Initial attempts to correlate the peak fluorescence emission intensity of the validation samples with the field portable TRPH data from MCTS yielded no apparent correlation. A potential explanation for the observed lack of relationship

between the fluorescence emission intensity and the TRPH data for the MCTS is that the coal tar may have partitioned into different chemical phases over time. Also, EPA Method 418.1 is known to yield low results for the highly aromatic organic compounds that comprise the majority of coal tar (Douglas et al. 1992).

SCAPS penetration data indicated a layer of contamination on top of the water table and another resting on a clay confining layer below the water table. Further, these two phases had distinctly different fluorescence emission spectra (Figure 4). These data indicate the presence of different chemical contaminants at various depths and locations at this site. It should be noted that the contingency analysis (Table 1) indicated good agreement between the LIF and TRPH measurements for MCTS. No linear correlation between TRPH and fluorescence response was observed for the samples collected at this site. However, the different contaminant types do appear to have different LIF response per unit TRPH contamination. The contaminant with a peak fluorescence at about 400 nm generally has a higher fluorescence response per unit TRPH than either of the other two contaminants. Another observation is that the contaminant with peak fluorescence response > 500 nm has extremely low fluorescence response per unit TRPH. The contaminant with a peak fluorescence response near 470 nm has fluorescence response per unit TRPH that is intermediate between the other contaminant types. The data obtained from the MCTS demonstrate the SCAPS POL sensor capability to differentiate multiple contaminants present at a given site in-situ and in real time.

SUMMARY

The objectives of this study were to develop a field portable TRPH procedure and investigate its utility for on site verification and calibration of the SCAPS POL sensor LIF response. Results of laboratory and field studies of soils contaminated with different POLs indicated that the field portable TRPH procedure was capable of providing data that was equivalent to that provided by EPA Method 418.1.

The field portable TRPH procedure was used at six field sites to validate the SCAPS POL sensor LIF response. The high percentage of true positives and low number of false negatives observed in the data obtained during this study support the utility of the SCAPS POL sensor for rapid site screening. The false positive LIF responses in this data set illustrate the need for an on-site method to identify non-POL fluorescence. Research currently underway to develop software based spectral identification of mineral fluorescence should eventually eliminate this problem. However, the data presented here indicate that, until this software is available, the field portable TRPH procedure developed here can reliably identify these false positive LIF responses.

The potential utility of the field portable TRPH procedure for on site calibration of the SCAPS POL sensor was illustrated for two sites contaminated with #2 diesel fuel. Linear correlations between LIF response and TRPH were observed for these sites. Sites with complex stratigraphy and multiple, complex contaminants (coal tar and refinery waste) did not yield simple correlations between TRPH and LIF response. However, the SCAPS POL sensor was able to identify the spatial distribution of different contaminants at a single site based on their fluorescence emission spectra.

More research is needed to understand the basic phenomenon that control the fluorescence response of POL products in varying soil matrices under field conditions. These phenomenon must be understood if the LIF response of petroleum contaminants in soils is to be utilized for more quantitative site characterization.

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Table 1. Summary of contingency analysis between field portable TRPH and LIF response for six field sites. The designation of true positive (+), true negative (-), false positive (\oplus) and false negative (\ominus) is discussed in detail in the text.

Designation	+	\oplus	-	\ominus
Fluorescence				
Sierra AD	7	12	2	1
Alameda NAS	22	12	9	0
Marshalltown	16	2	5	2
Atlantic	18	2	18	8
York	26	3	21	4
Ft. Riley	21	0	13	3
Totals	110	31	68	18
TRPH				
Sierra AD	8	(1)	14	(1)
Alameda NAS	22	21		
Marshalltown	18	7		
Atlantic	25	21		
York	31	23		
Ft. Riley	24	13		
Totals	128	99		
Percentage, fluorescence of TRPH	86	31	69	14

(1) The TRPH values measured for soil samples is always considered to be correct. Therefore, no false positive or false negative TRPH values are possible.

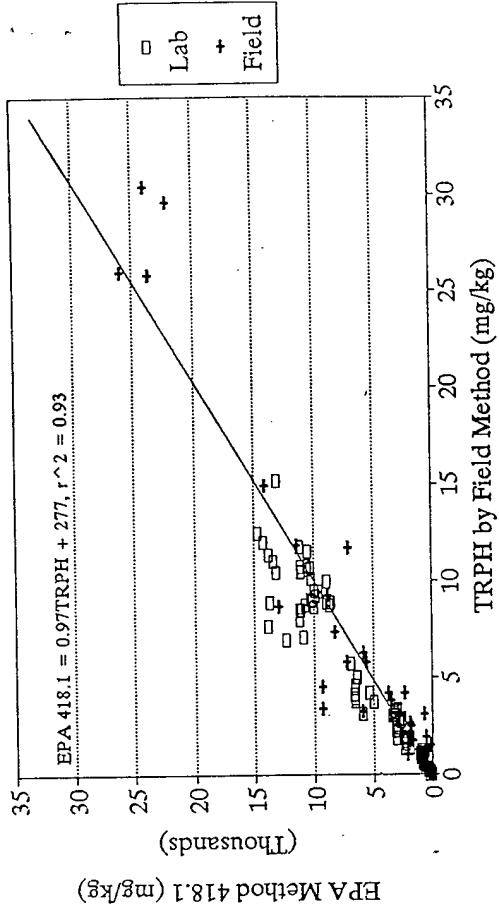


Figure 1. Relationship between field portable TRPH and EPA Method 418.1 Pooled data ($n = 298$) for laboratory spiked and field contaminated soils.

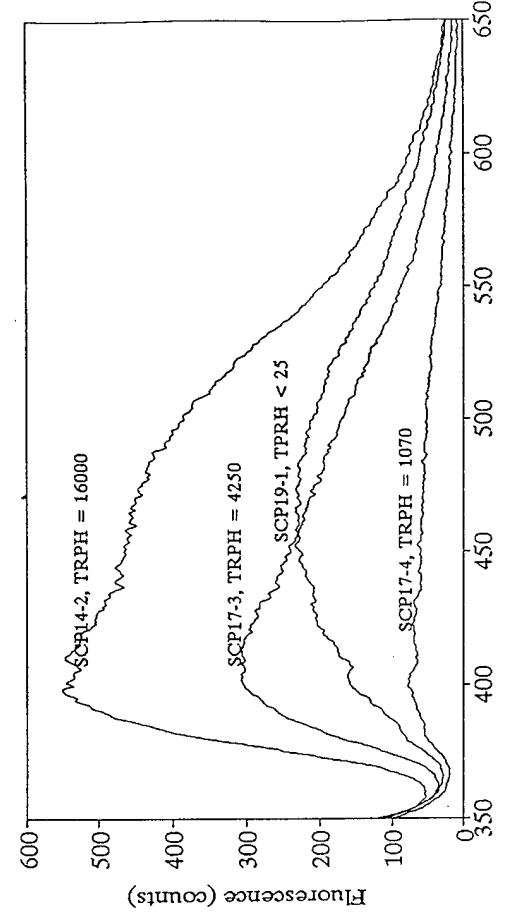


Figure 2. Fluorescence emission spectra for selected validation samples collected at Sierra Army Depot. The spectra of samples 14-2, 17-3 and 17-4 are typical for #2 diesel fuel. The spectrum of sample 19-1 is assumed to be that of calcite.

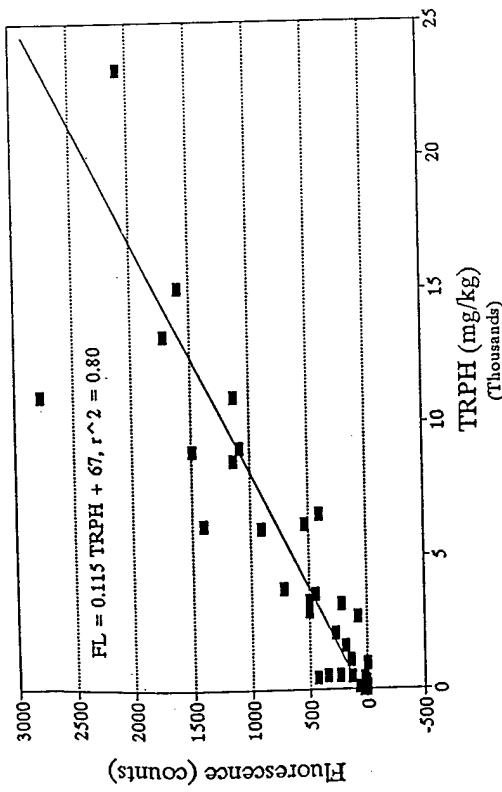


Figure 3. Fluorescent response of validation samples obtained at Ft. Riley #2 diesel site. TRPH measurements were carried out using the field portable procedure.

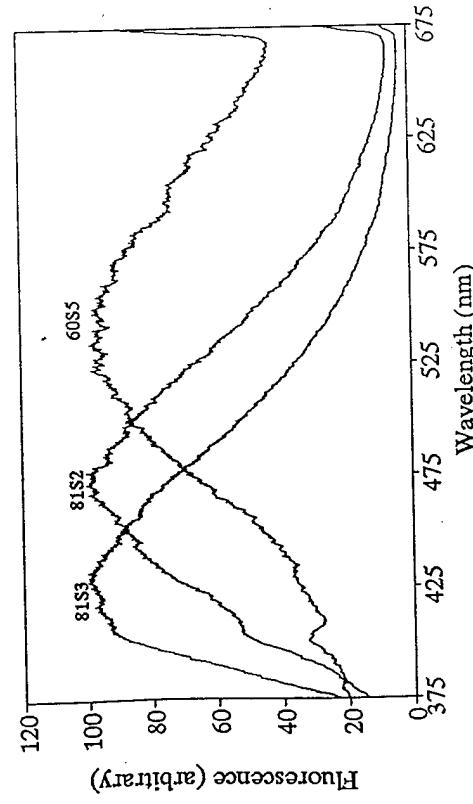


Figure 4. Fluorescence emission spectra of selected validation samples collected at the Marshalltown Coal Tar Site.